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Thermal, spectroscopic studies and hydrogen bonding in supramolecular assembly of azo rhodanine complexes

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ABSTRACT

A novel series of Cu(II) complexes of azo rhodanine derivatives (HL_n) have been prepared and characterized by thermal analysis, spectral studies (IR, mass, UV–Vis, ESR) and magnetic measurements. IR spectra suggest that the HL_n acts as a bidentate ligands coordinating *via* (N=N) and deprotonated enolized carbonyl oxygen (–C–O–). ESR spectra of the Cu(II) complexes show d_{x2-y2} as a ground state, suggesting tetrahedral distorted or square planar geometries around Cu(II) center. The X-ray diffraction (XRD) patterns powder forms of Cu(II) complexes shows many diffraction peaks which indicates the polycrystalline phase. Thermal properties and decomposition kinetics of compounds are investigated. The thermodynamic parameters and evaluation of kinetic parameters (E_a, ΔS^*, ΔH^* and ΔG^*) of thermal decomposition stages have been evaluated using Coats–Redfern and Horowitz–Metzger methods. Cu(II) complexes are screened for their biological activity against bacterial and fungal species. The Cu(II) complexes showed antimicrobial activities against *Staphylococcus aureus* and *Penicillium italicum*.

1. Introduction

Azodyes are an important class of organic colorants which consist of at least a conjugated chromophore azo (—N=N—) group and the largest and most versatile class of dyes. It has been known for many years that azo compounds are the most widely used class of dyes due to their versatile application in various fields such as the dyeing of textile fiber and coloring of different materials, and for plastics, biological-medical studies, and advanced applications in organic synthesis [1–4].

Over the past decades, azodyes and their transition metal complexes have made significant contribution in the development of co-ordination chemistry. The most important step in the development of metal complexes was perhaps the preparation of a new ligand which exhibit unique properties and novel reactivity. Since, the electron donor and electron acceptor properties of the ligand, structural functional groups and the position of the ligand in the coordination sphere together with the reactivity of coordination compounds may be a factor of different studies [4–6]. Azodyes metal complexes have been studied extensively [6–9] because of their attractive chemical and physical properties and their wide range of applications such as catalysts, antimicrobials and corrosion inhibitors. The presence of the nitrogen atoms of the azo group makes the azodyes more significant chemically and biologically [5,10].

Azo compound based on rhodanine, play a central role as chelating agents for a large numbers of metal ions, as they form a stable six- member ring after complexation with a metal ion and also it could be used as analytical reagents [11,12]. The complex-formation equilibrium have been reported for several kinds of rhodanine derivatives [4,13–15]. Potentiometry, conductivity and spectroscopy measurements on the coordination ability biologically important azo derivatives have shown that their complexes are very stable [16–18].

In this present study, we report the synthesis, characterization of Cu(II) complexes of azo rhodanine derivatives ligands (HL_n). The structure of the isolated complexes is elucidated using elemental analyses, IR, mass spectra, magnetic moment, ESR and thermogravimetric analysis. The activation thermodynamic parameters were calculated using Coats–Redfern and Horowitz–Metzger methods. Study of the antimicrobial activities of Cu(II) complexes.

2. Experimental

All the chemicals used were of British Drug House quality.

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2.1. Synthesis of 5-(4′-derivatives phenylazo)-2-thioxothiazolidin-4-one (HL_n)

In a typical preparation, 25 ml of distilled water containing 0.01 mol hydrochloric acid were added to aniline (0.01 mol) or *p*-derivatives. To the resulting mixture stirred and cooled to 0 °C, a solution of 0.01 mol sodium nitrite in 20 ml of water was added dropwise. The formed diazonium chloride was consecutively coupled with an alkaline solution of 0.01 mol 2-thioxo-4-thiazolidinone, in 10 ml of pyridine. The colored precipitate, which formed immediately, was filtered through sintered glass crucible, washed several times with water and ether then dried in a vacuum desiccator over P_2O_5. The elemental analysis of the ligands (HL_n) are given in Table 1.

2.2. Preparation of the complexes

$CuCl_2{\cdot}2H_2O$ (0.01 mol) in 30 ml ethanol was added to a solution of HL_n (0.01 mol) in 30 ml ethanol. The mixture was then refluxed on a water bath for ~4 h and allowed to cool whereby the solid complexes were separated, which filtered off, washed several times with ethanol, the solid was dried in a vacuum desiccator over P_2O_5.

2.3. Biological activity investigation

For this investigation the agar well diffusion method was applied [5,10]. The antibacterial activities of the investigated compounds were tested against two local Gram positive bacterial species (*Bacillus cereus* and *Staphylococcus aureus*) and two local Gram negative bacterial species (*Escherichia coli* and *Klebsiella pneumoniae*) on nutrient agar medium. Also, the antifungal activities were tested against four local fungal species (*Aspergillus niger*, *Alternaria alternata*, *Penicillium italicum* and *Fusarium oxysporum*) on DOX agar medium. The concentrations of each solution were 150, 100 and 50 μg/ml in dimethyl formamide (DMF). By using a sterile cork borer (10 mm diameter), wells were made in agar medium plates previously seeded with the test microorganism. 200 μl of each compound was applied in each well. The agar plates were kept at 4 °C for at least 30 min to allow the diffusion of the compound to agar medium. The plates were then incubated at 37 °C or 30 °C for bacteria and fungi, respectively. The diameters of inhibition zone were determined after 24 h and 7 days for bacteria and fungi, respectively, taking the consideration of the control values (DMF). Penicillin and miconazole were used as reference substances against bacteria and fungi, respectively.

Table 1
Elemental analysis (C, H, N and S) and physical data of the ligands (HL_n).

Compound[a]	Color	Yield (%)	m.p. (°C)	Experimental (calc.) (%)			
				C	H	N	S
HL_1	Red	37.45	221	44.82 (44.93)	3.25 (3.39)	15.85 (15.72)	23.65 (23.97)
HL_2	Dark Orange	47.81	231	47.88 (47.79)	3.76 (3.61)	16.61 (16.72)	25.23 (25.50)
HL_3	Pale Yellow	42.19	237	45.68 (45.55)	2.80 (2.97)	17.85 (17.71)	26.78 (27.00)
HL_4	Light Orange	51.37	248	39.65 (39.78)	2.35 (2.23)	15.58 (15.46)	23.24 (23.57)
HL_5	Dark Yellow	66.09	245	38.42 (38.29)	2.25 (2.14)	19.98 (19.85)	22.55 (22.70)

[a] The analytical data agree satisfactory with the expected formulae represented as given in structures HL_1–HL_5. Air-stable, colored, insoluble in water, but soluble in hot ethanol, and soluble in coordinating solvents.

2.4. Analytical and physical measurements

Elemental microanalyses of the separated compounds for C, H, N and S were determined on Automatic Analyzer CHNS Vario ELIII, Germany. The analyses were repeated twice to check the accuracy of the analyzed data. The ^1H NMR spectra were obtained with a JEOL FX90 Fourier transform spectrometer with DMSO-d_6 as the solvent and TMS as an internal reference. The infrared spectra were recorded as KBr discs using a Perkin-Elmer 1340 spectrophotometer. Mass spectra were recorded by the EI technique at 70 eV using MS-5988 GS-MS Hewlett-Packard. X-ray diffraction analysis of complexes powder forms was recorded on X-ray diffractometer in the range of diffraction angle $2\theta° = 4–70°$. This analysis was carried out using Cu Kα radiation ($\lambda = 1.540598$ Å). The applied voltage and the tube current are 40 kV and 30 mA, respectively. Ultraviolet–Visible (UV–Vis) spectra of the compounds were recorded in nuzol solution using a Unicom SP 8800 spectrophotometer. The magnetic moment of the prepared solid complexes was determined at room temperature using the Gouy's method. Mercury(II) (tetrathiocyanato)cobalt(II), $[Hg\{Co(SCN)_4\}]$, was used for the calibration of the Gouy tubes. Diamagnetic corrections were calculated from the values given by Selwood [19] and Pascal's constants. Magnetic moments were calculated using the equation, $\mu_{eff.} = 2.84\ [T\chi_M^{coor.}]^{1/2}$. Thermal studies were computed on Simultaneous Thermal Analyzer (STA) 6000 system using thermogravimetric analysis (TGA) method. Thermal properties of the samples were analyzed in the temperature range from 30 to 800 °C at the heating rate of 10 °C/min under dynamic nitrogen atmosphere. ESR measurements of powdered samples were recorded at room temperature using an X-band spectrometer utilizing a 100 kHz magnetic field modulation with diphenyl picrylhydrazyle (DPPH) as a reference material. The conductance measurement was achieved using Sargent Welch scientific Co., Skokie, IL, USA.

3. Results and discussion

3.1. Stoichiometry of the copper(II) complexes

The stoichiometry of the complexes have been deduced from their elemental analysis (Table 2), which indicates that the metal complexes fall into 1:1 (monomeric) (metal:ligand). The ligands (HL_n) are mononucleating and hence require one metal ion for coordination. All the products were partially soluble in common

Table 2
Elemental analysis data of Cu(II) complexes[a] (for molecular structure see Fig. 2).[b]

Complex[c]	Experimental (calc.) (%)				Cl
	C	H	N	S	
$[Cu(L_1)(OH_2)Cl]$ (**1**)	31.14 (31.33)	2.45 (2.61)	10.76 (10.97)	16.44 (16.71)	9.11 (9.27)
$[Cu(L_2)(OH_2)Cl]H_2O$ (**2**)	31.04 (31.17)	2.52 (2.60)	10.66 (10.91)	16.44 (16.62)	9.01 (9.22)
$[Cu(L_3)(OH_2)Cl]$ (**3**)	30.46 (30.59)	2.16 (2.27)	11.67 (11.90)	18.02 (18.13)	9.88 (10.06)
$[Cu(L_4)(OH_2)Cl]H_2O$ (**4**)	26.59 (26.63)	1.66 (1.73)	10.06 (10.36)	15.52 (15.78)	16.89 (17.51)
$[Cu(L_5)(OH_2)Cl]H_2O$(**5**)	25.83 (25.96)	1.55 (1.68)	13.13 (13.46)	15.19 (15.38)	8.42 (8.53)

[a] Microanalytical data as well as metal estimations are in good agreement with the stoichiometry of the proposed complexes, air stable, non-hydroscopic, high melting temperature and colored.

[b] The excellent agreement between calculated and experimental data supports the assignment suggested in the present work.

[c] L_n are the anions of the ligands (HL_n).